ORIGINAL ARTICLE

Seasonal Variations of Natural Organic Matter (NOM), Residual Chlorine, and pH in Water Distribution Networks of Shiraz City

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Abstract

Background: Natural Organic Matters (NOMs) react in the presence of residual chlorine in distribution network pipes, producing such byproducts as Trihalomethanes which are carcinogenic and mutagenic. The present study was conducted to investigate the quality of drinking water in Shiraz.
Methods: In this cross-sectional study, 54 samples were taken from 27 locations in both summer and winter. For each sample, temperature, residual chlorine, pH, and NOM were measured during the two seasons. Residual chlorine and temperature measurement were performed at the sampling sites, but pH and NOM were measured in the laboratory.
Results: According to the results, the mean concentrations of Total NOM (TNOM), residual chlorine, pH, and temperature varied from 0.9 to 5 m^{-1}, 0 to 1.2 mg/L, 7.4 to 8 and 18 to 23.5 ^{o}C in summer and from 0.3 to 1.5 m^{-1}, 0 to 0.8 mg/L, 7.6 to 8.2 and 9.7 to 10.8 ^{o}C in winter, respectively. In addition, the concentrations of all measured parameters, except for pH, were reported to be higher in summer than in winter.
Conclusion: As a result, since the amount of NOM in the drinking water distribution network of Shiraz was not zero, regular monitoring of these compounds in the distribution networks is recommended to be done by engineers.

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Introduction

As population density increases, the demand for healthy water increases; also, the quality and quantity of drinking water are of paramount importance for human health.[1, 2] The treated water enters the distribution pipes after leaving the treatment plant. This water goes a long way in the pipes to be accessible to the consumers. Therefore, the major concerns are the problems and reactions that may occur along the pipes.[3, 4] One of the main concerns in the drinking water distribution network is the Natural Organic Matters (NOMs),[5] which is generally found in surface and ground water. NOM is a wrapped combination of organic materials with diverse weights and specifications,[1] for example humic substances, carbohydrates, amino acids, and carboxylic acid.[6] NOM can be available in dissolved form (DOM: Dissolved Organic Matter) or as a particle (POM: Particle Organic Matter), and it is more difficult to remove the first type from water.[7]

Corpse of animals, plants, microorganisms, and even wastes can be a source of NOM, which is the reason why it can be found in natural sources, such as water, soil, and sediments.[1] NOM has also been considered as a key to water quality,[8] which can be created by biological, geological, and hydrological interactions in water.[9] It should be noted that the presence of NOM in surface and ground water may vary depending on seasonal and spatial conditions.[1, 10]

Although NOM may not be harmful by itself, it causes water quality problems,[11] such as undesirable colors, flavors, and odor,[1, 12] and increased costs due to the increased coagulant rate that results in more sludge production.[12] Change in the color of water refers to the darkening of water, indicating an increase in the concentrations of organic matters.[13] In addition, NOM removal in water treatment plants may result in the formation of byproducts (DBPs) during the treatment process or before and after chlorination.[1] DBPs are generally formed by the reaction of disinfectants such as chlorine with natural organic matter in source water and NOM acts as a forerunner to DBPs.[1] The most important byproducts detected in drinking water are Haloacetic Acids (HAAs) and Trihalomethanes (THMs).[8, 14] In the recent years, many studies have been conducted on the formation of new aromatic halogenated DBPs from NOM with chlorine composition.[15] Based on the results, DBPs, such as THMs, could pose a serious threat to human health due to their carcinogenicity and mutagenicity.[8, 15] Bromide concentration, Dissolved Organic Carbon (DOC), NOM, temperature changes, chlorine concentration, pH, and contact time have been found to be the most important parameters for the formation of DBPs, such as THMs.[16, 17] Moreover, previous studies demonstrated that the values measured in UV_{254}, Total Organic Carbon (TOC), and DOC could represent NOM, which implies that NOM is significantly related to these parameters.[14, 18]

Up to now, numerous studies have measured NOM in groundwater,[19] lake and river water,[8, 20] and during various processes of treatment plants.[21] In addition, THMs have been often measured in distribution networks.[22, 23] Most engineers have focused on the removal of NOM in treatment plants and have ignored the presence of NOM in distribution networks. In Shiraz, also, despite the removal of NOM in treatment plants, NOM is quite likely to exist in water due to the erosion of the distribution pipes as well as different genders of the pipes; it reacts with disinfectants, such as chlorine, and is considered a source of DBPs. Given the serious hazards and lack of any studies related to NOM in water distribution networks, the present study was designed to determine the amount of NOM (measured as UV_{254}) in drinking water in two hot and cold seasons in Shiraz, Iran.[24]

Methods

Characteristics and Location of the Study Area

Shiraz, with a population of more than 1.8 million, is the capital of Fars province and the fifth most populous city of Iran. The city is located in the southwest of the country and has a moderate climate.[25] It is also one of the oldest cities in ancient Iran. Petrochemical and electronics industries are among the most important economic activities in Shiraz, while agriculture and tourism also play an important role in the economy of this city.[24, 26, 27] In this study, Shiraz was divided into 10 regions and a code was assigned to each region. The number of samples taken from each area was considered according to the relative population of that area (Table 1). According to Figure 1, sampling was performed in 27 regions during summer (from September 6 to September 12) and winter (from February 10 to February19), and finally 54 samples were collected. It should be noted that the samples were taken directly from taps at homes, shops, schools, etc.

Table 1: The number of samples

Region	Code of region	Number of samples
1	A	4
2	B	3
3	C	3
4	D	4
5	E	3
6	F	2
7	G	3
8	H	1
9	I	2
10	J	2
Total	-	27

Sampling Method

Before sampling, the bottles used for sampling were washed with deionized water and detergent in the laboratory and were then dried at 400°C.[28] In each sampling area, the faucet was first opened for three to five minutes to drain the water directly from the distribution network. After that, the sampling bottles were rinsed several times with the sample water and finally filled completely with the sample water.[28] After sampling, the bottles were covered with aluminum foil and immediately transferred to laboratory in ice boxes for NOM analysis. It should be mentioned that residual chlorine measurement (DPD tablet for measuring the residual chlorine sample from Arakshimi company) and temperature measurement (thermometer) were performed at the sampling sites.[19]

In the laboratory, the pH of the samples was measured using a pH meter (pH 827 model of the Swiss Metro company). For NOM analysis, the samples were first kept at room temperature for two hours to equalize the temperature. Then, the pH of all samples was adjusted to 7 using 1 M HCl. Finally, the samples were poured into quartz cells once before filtration (Total NOM=TNOM) and once by going through a 0.45 µm membrane filter to remove the particles (Dissolved NOM=DNOM); also, the absorption rate was measured using the standard method 5910 B by a spectrophotometer (HACH DR 5000) at a wavelength of 254 nm.[7, 8, 20] Particle NOM

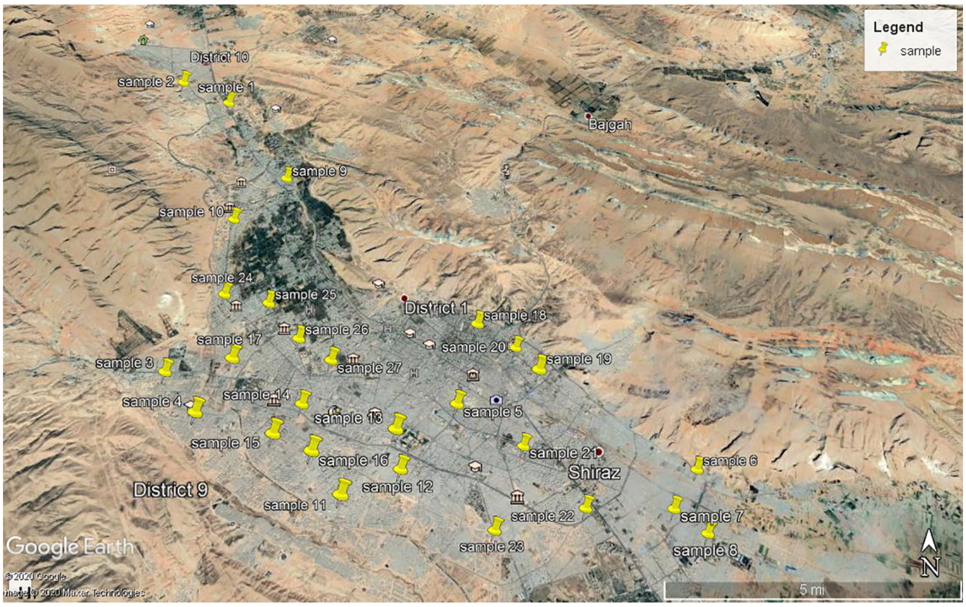

Figure 1: Map of the sampling sites

(PNOM) was also calculated from the difference between TNOM and DNOM. It should be noted that the device was first zeroed by the control sample, which was deionized water. Although the results obtained from UV absorption were expressed in cm^{-1}, they were reported in m^{-1} in this study.

Statistical Analysis

The data were analyzed using the SPSS software, version 23. The normality of NOM, pH, residual chlorine, and temperature was tested using one-sample Kolmogorov-Smirnov test. In addition, the differences in the mean concentrations of all parameters were determined using a non-parametric test, Mann-Whitney U Test. In addition, The Spearman's Rank Correlation Coefficient was used to discover the strength of a link between the two variables.

Results

Water Distribution Network Characteristics

The average results of the measured water quality parameters and NOM of drinking water in each region in the two seasons are presented in Table 2. In addition, the comparison of the 10 regions in the two seasons is illustrated in Figure 2. In summer, the values of TNOM, residual chlorine, pH, and temperature varied from 0.9 to 5 m^{-1}, 0 to 1.2 mg/L, 7.4 to 8, and 18 to 23.5 ^{o}C, respectively. In winter, the values of TNOM, CL, pH, and temperature varied from 0.3 to 1.5 m^{-1}, 0 to 0.8 mg/L, 7.6 to 8.2, and 9.7 to 10.8 ^{o}C, respectively.

Seasonal Variations of the Levels of the Measured Parameters in the Water Distribution Network

The seasonal changes in the average concentrations of the parameters measured in drinking water are shown in Figure 3.

Difference between PNOM and DNOM

Since NOM can be present in both dissolved (DNOM) and particle (PNOM) forms in water, the difference between PNOM and DNOM is presented in Figure 4.

Table 2: The measured parameters in the drinking water distribution network from 10 areas

Parameters Area	Seasons											
	Summer						Winter					
	TNOM (m^{-1})	DNOM (m^{-1})	PNOM (m^{-1})	CL (mg/L)	pH	T C^0	TNOM (m^{-1})	DNOM (m^{-1})	PNOM (m^{-1})	CL (mg/L)	pH	T C^0
Area 1	2.1	0.7	1.4	0.7	7.9	20.4	0.9	0.5	0.4	0.8	8.1	10.2
Area 2	2.7	0.8	1.8	0	7.6	18	1	0.8	0.2	0	7.7	9.7
Area 3	2.7	1.4	1.2	0.2	7.6	19	0.8	0.5	0.2	0	7.9	10.8
Area 4	3	1.8	1.2	0.2	7.9	20.5	1.3	0.6	0.6	0.5	8.2	10
Area 5	5	1.9	3.1	0	7.8	19.3	0.8	0.2	0.6	0	7.9	9.8
Area 6	2.1	1.9	0.2	1.2	8	23.5	1.5	0.4	1.1	0.5	8.2	9.9
Area 7	2	1.2	1.1	0.5	7.9	20.4	0.7	0.5	0.2	0.1	7.8	10.7
Area 8	0.9	0.2	0.7	0.3	7.4	20	0.4	0.1	0.3	0.1	7.6	10.3
Area 9	2.9	2.4	0.5	0	8	20.4	0.7	0.4	0.2	0.7	8	10
Area 10	2.3	1.2	1.1	0.5	7.9	20.4	0.3	0.1	0.2	0	8	9.9

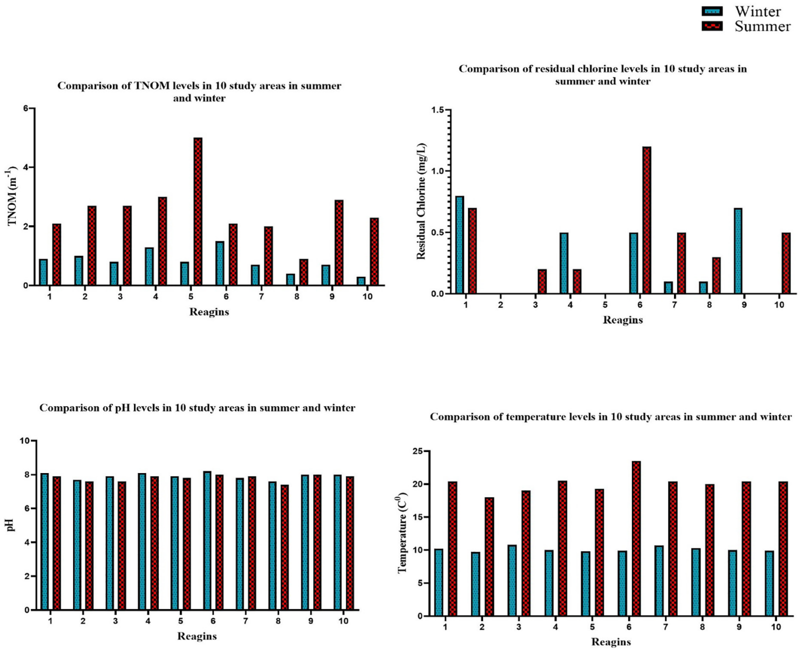

Figure 2: Measured parameters in the study areas

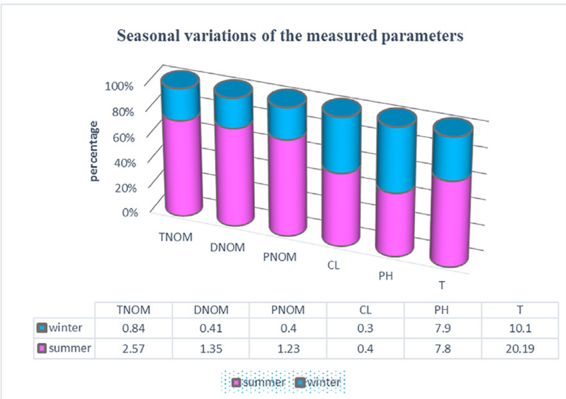

Figure 3: Seasonal variations of the measured parameters levels in the water distribution network

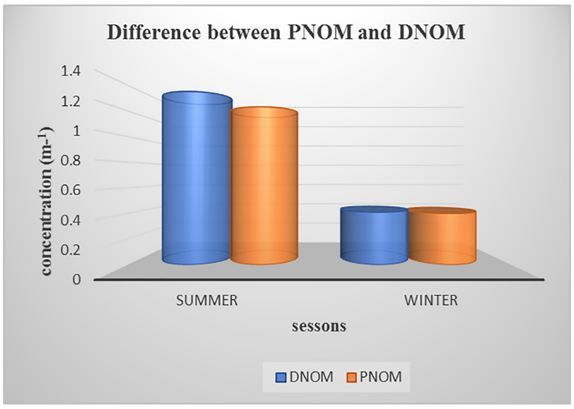

Figure 4: Difference between PNOM and DNOM

The Correlations among the Measured Parameters

The correlations among the values of the measured parameters in the 54 samples are shown in Table 3.

Discussion

In this study, based on the results, the pH of Shiraz drinking water in the distribution networks ranged from 6.5 to 8.5, which was within the threshold of the desired limit declared by the World Health Organization (WHO).[29] In addition, according to Figure 2, water of region 6 had the highest pH compared to other regions in both seasons, which could be due to treatment breakdowns, accidental spills, and insufficiently cured cement mortar pipe linings.[29]

Although the chlorine in water distribution pipes protects the system against possible contaminations, especially microorganisms, large amounts of chlorine cause unpleasant odor and taste in the water, which will discourage people from drinking. Therefore, according to WHO recommendations, the amount of residual chlorine should be between 0.2 and 0.5 mg/l.[30] However, the amount of residual chlorine in regions 2 and 5 was reported to be zero in both seasons, which was lower than the recommended value. On the other hand, the amount of chlorine reported in region 6 (1.2

Table 3: Spearman coefficient between the measured parameter.

	Residual chlorine	pH	TNOM	T
Residual chlorine	1.000	0.304*	0.005	0.214
PH	0.304*	1.000	-0.075	-0.101
TNOM	0.005	-0.075	1.000	0.602**
T	0.214	-0.101	0.602**	1.000

mg/l) was higher than the recommended amount. Therefore, the amount of residual chlorine could be worrying in both cases.

In our study, the highest values of TNOM measured in summer (5 m^{-1}) and winter (1.5 m^{-1}) were reported in regions 5 and 6, respectively. In addition, the amount of NOM in Shiraz water distribution network was between 0.3 and 5 m^{-1}, which was inconsistent with the results of a study conducted on the drinking water distribution network in central eastern Sweden)4-8 m^{-1} (.[4] This discrepancy in the results could be due to the differences in the path length pollutants of the water distribution network or the differences in the treatment process in the treatment plants. Another study was conducted on the raw water of three rivers, namely Lar, Jajrood, and Karaj, in Iran, indicating that the average NOM was 20.1, 49.9, and 35.9, respectively.[20] These values were significantly higher compared to those obtained in the present investigation, which demonstrated that the NOM range was acceptable in Shiraz water distribution network.

According to the results, the average pH of drinking water was higher in winter than in summer, which was inconsistent with the results of a study carried out in Nigeria Lake, in which the average pH was higher in hot seasons than in cold seasons, but this difference was not significant ($P>0.05$).[31] This difference might be associated with the variations in the types of water source. However, a study on pure water revealed that the pH decreased with increase in temperature, which was in agreement with the results of the current investigation.[32] Furthermore, the residual chlorine in the drinking water distribution network of Shiraz was higher in summer than in winter ($P>0.05$), which was in line with a study conducted on Sanandaj water distribution network, Iran[33] and another research performed on the water distribution system in Samarra, Iraq.[34] The higher amount of residual chlorine in summer could be due to the fact that Shiraz Water and Sewerage Company adds more chlorine to water during summer. Moreover, the results indicated that TNOM was significantly higher in summer than in winter ($P<0.05$). A previous study carried out on waters of rivers in Iran indicated that the value of NOM increased by moving towards warmer seasons.[20] The results of a study conducted in South Africa also showed that increased rainfall followed by increased water flow was accompanied by an increase in the amount of NOM.[21] In the same vein, the present study results indicated an increase in rainfall and a decrease in NOM in winter compared to summer.

Based on the results of the current study, DNOM was higher than PNOM in both seasons. Since the former was higher in the water distribution network of Shiraz, it was more difficult to remove NOM.

As shown in Table 3, there was a correlation between residual chlorine and pH. There was also a significant correlation between temperature and TNOM. The results of a study on Sanandaj water distribution network also revealed a significant relationship between residual chlorine and pH.[33]

Conclusion

According to the reported results, the amounts of residual chlorine and NOM were high in Shiraz drinking water distribution network during summer. Therefore, there is a greater concern about the formation of byproducts, such as THMs, in summer than in winter. Since no limit values were found for NOM according to standard guidelines, the results were compared to those of the previous investigations conducted on various sources. Fortunately, NOM measured in the two seasons was lower in comparison to other studies. Although the amount of NOM in Shiraz drinking water distribution network in the two seasons studied did not seem to be worrying, it could not guarantee all months and years, because the amounts of natural organic compounds in the drinking water distribution network were not zero. Therefore, engineers are recommended to pay attention to the presence of these compounds in distribution networks and focus on their elimination in the water.

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Conflicts of interest*:* None declared.

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